Polymer Multiphase Materials Group

Phase Diagram Measurement of Polyolefin Blends with Nearly Iso-refractive Components

Olefin blends are most widely used plastic materials. During the processing, the mixtures undergo both liquid-liquid phase separation and crystallization, complicating the morphology hence the property control of the final product. It is critical to measure the phase diagram in order to understand the driving force of the morphology formation. We developed novel approaches for determining the phase diagram of polyolefin blends with nearly iso-refractive components.

The Polyolefin Statistical Copolymers

PEH: ethylene/hexene

$[-CH_2-CH_2-]_x[-CH_2-CH-]_{1-x}$ with CH_2, CH_2, CH_2, CH_3 side groups

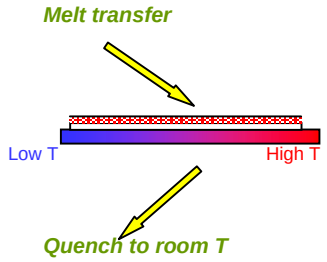
M_w=110k g/mol
x = 0.98
ρ_{branch}: 1/57 backbone C

PEB: ethylene/butene

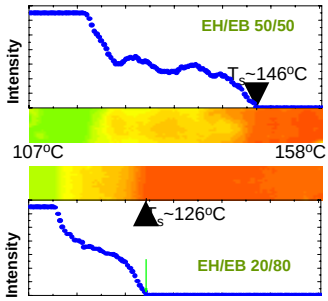
$[-CH_2-CH_2-]_x[-CH_2-CH_1-]_{1-x}$ with CH_2, CH_3 side groups

M_w=70k g/mol
x = 0.86
ρ_{branch} : 1/13 backbone C

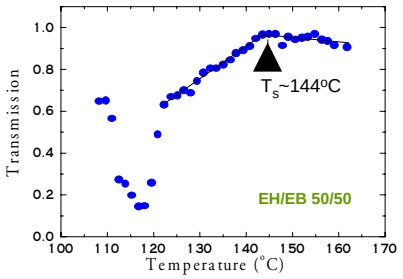
Anneal a film of blend on a temperature gradient hot stage and quench to room temperature.



Characterization I: photography

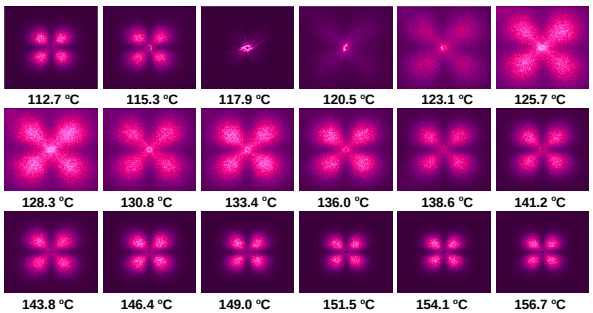


Characterization II: light transmission

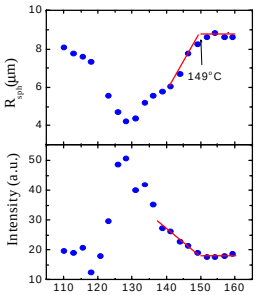


Characterization III: de-polarized small angle light scattering

H_v Scattering Patterns of 50/50 Blend

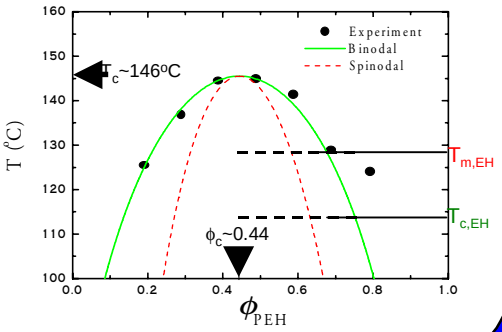


Quantification

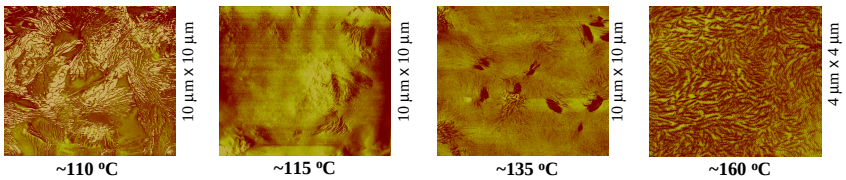


Phase Diagram of PEH/PEB Blend

$\chi = -5.5 \times 10^{-4} + 0.5/T$



Characterization IV: Atomic Force Microscopy



The pre-introduced liquid-liquid phase separation affects the consequent crystallization morphology, giving contrast for determining the phase boundary in a mixture of iso-refractive polyolefins in the melt state.

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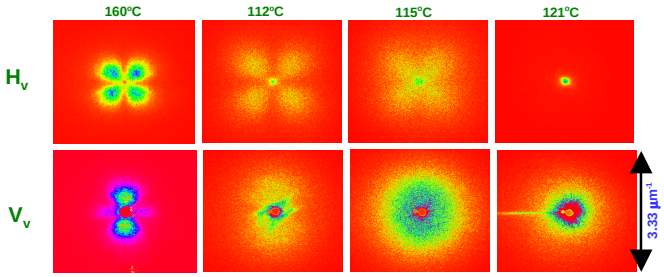
Characterizing the Morphology Development in Short-chain-branched Polyethylene Blends

Polymer Multiphase Materials Group

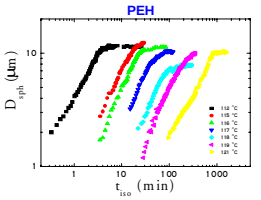
A variety of techniques have been used to characterize the morphology development in blends of poly(ethylene-co-hexene) and poly(ethylene-co-butene) statistical copolymers, including optical microscopy (OM), small angle light scattering (SALS), atomic force microscopy (AFM) and simultaneous small angle and wide angle X-ray scattering (SAXS and WAXS).

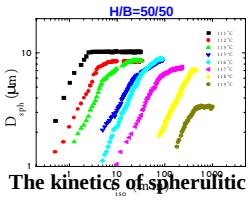
H/B=50/50, quench to rm T from various temp. (SALS)

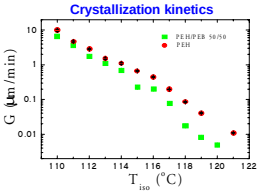


The morphology crossover from spherulitic growth dominant to phase separation dominant with decreasing undercooling.

Sperulites growth kinetics (OM)



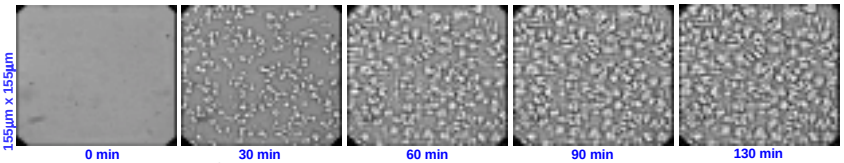




The kinetics of spherulitic growth indicates change of crystallization mechanism at *ca.* 115 °C, below which the growth rate G_{PEH}~1.5 G_{HB} at different degrees of undercooling. The constant suppression of growth rate is mainly due to the dilution effect.

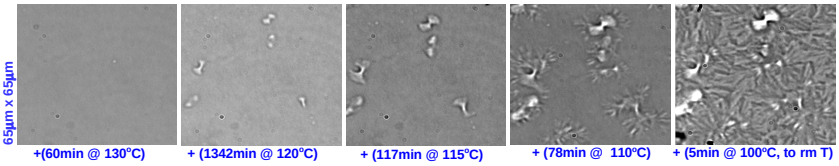
At high temperatures, the growth kinetics indicates the effects of both the composition and degree of undercooling. The ratio G_{PEH}/G_{HB} increase with decreasing undercooling.

EH/EB=90/10, isothermal crystallization at 115°C (OM)



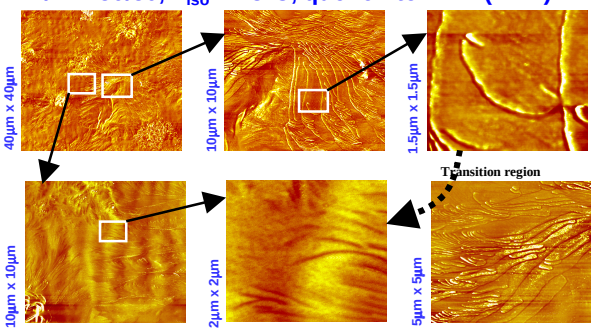
Observation of the spherulitic morphology and its growth kinetics in blends.

EH/EB=50/50, stepwise annealing after at 160°C for 5 min (OM)



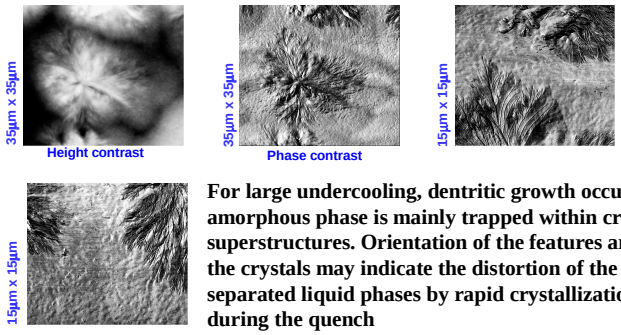
Change of crystallization mechanisms results in different morphology.

EH/EB=50/50, T_{iso}=118°C, quench to rm T (AFM)



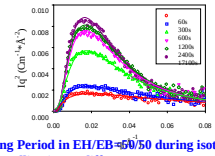
For isothermal crystallization at small undercooling, well-defined lamella grow and the amorphous phase is driven to the interspherulitic region.

EH/EB=50/50, T_{iso}=113°C, 10 min, quench to ice water (AFM)

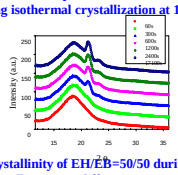


For large undercooling, dentritic growth occurs. The amorphous phase is mainly trapped within crystal superstructures. Orientation of the features around the crystals may indicate the distortion of the separated liquid phases by rapid crystallization during the quench

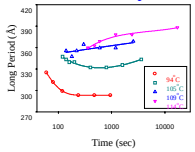
Selected SAXS profiles of EH/EB=50/50 during isothermal crystallization at 114°C



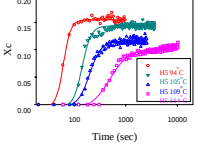
Selected WAXS profiles of EH/EB=50/50 during isothermal crystallization at 114°C



Long Period in EH/EB=50/50 during isothermal crystallization at different temperatures.



Crystallinity of EH/EB=50/50 during isothermal crystallization at different temperatures.



Time resolved simultaneous SAXS and WAXS measurements during isothermal crystallization provide dynamic information such as the evolution of the lamellae long period and crystallinity for various degrees of undercooling and blend compositions. The average property from the scattering techniques are related to morphology details.

The morphology development in the PEH/PEB blends is controlled by many factors, such as ratio of crystallizable to amorphous component, quench depth, degree of undercooling, duration of annleaing and thermal history. It is necessary to combine different techniques to gather different facets of the complex phenomena.

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